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On the Order of Catalytic Isomerization

The curve between the concentration of a reactant or a product and time is, in general, used to yield information about the order of the reaction. The apparent first-order rate equation has been applied for the *ortho–para*-hydrogen conversion over γ-alumina (*1*), the isomerizations of 1-butene over Ce–Y zeolite (*2*), over silica-supported rhodium chloride (*3*), and over Type A zeolites (*4*), the isomerization of allene over silica-supported iron (*5*), and the isomerizations of methylcyclohexenes and of methylenecyclohexane over γ-alumina. The rate equation which has been applied to these reactions is expressed by

$$\ln\left\{\frac{P_0 - P_A{}^e}{P_A - P_A{}^e}\right\} = k\,t, \qquad (1)$$

where k is a time-independent constant, and P_0, $P_A{}^e$, and P_A are initial pressure, the equilibrium pressure, and the pressure of a reactant A at time t, respectively. The constants k which have been obtained from Eq. (1) differ from the rate constants of an ordinary chemical reaction. They are constant only for the course of an isomerization reaction with a single mixture of reacting gases, but they are dependent on total pressure and assume different values if the total pressures of the reaction are altered.

It is important to understand why this apparent first-order behavior is generally found for the course of an isomerization reaction with time and it is important to determine the condition under which the kinetic behavior is approximately expressed by Eq. (1). In the present paper, the rate equation for the catalytic isomerization is derived by assuming a reaction scheme and then the condition under which the rate equation derived is approximated by Eq. (1) is discussed.

The overall isomerization reaction defined by

$$A \rightleftarrows B \qquad (2)$$

is postulated to consist of the elementary reactions

$$A + S \underset{\overleftarrow{k}_a}{\overset{\overrightarrow{k}_a}{\rightleftarrows}} AS, \qquad (3a)$$

$$AS \underset{\overleftarrow{k}_b}{\overset{\overrightarrow{k}_b}{\rightleftarrows}} BS, \qquad (3b)$$

$$BS \underset{\overleftarrow{k}_c}{\overset{\overrightarrow{k}_c}{\rightleftarrows}} B + S, \qquad (3c)$$

where $\overrightarrow{k}_a$ and $\overleftarrow{k}_a$ are the rate constants for the forward and the reverse reactions in Eq. (3a), respectively. S and AS are the vacant site and the adsorbed A, respectively. Reactant A may adsorb competitively on the same site with product B because they have similar chemical properties. The overall equilibrium constant, K, and the adsorption equilibrium constants for reactant A, K_A, and for product B, K_B, may be written as

$$K = \frac{P_B{}^e}{P_A{}^e} = \frac{\overrightarrow{k}_a\overrightarrow{k}_b\overrightarrow{k}_c}{\overleftarrow{k}_a\overleftarrow{k}_b\overleftarrow{k}_c}, \qquad (4)$$

$$K_A = \frac{\overrightarrow{k}_a}{\overleftarrow{k}_a}, \qquad (5)$$

$$K_B = \frac{\overleftarrow{k}_c}{\overrightarrow{k}_c}, \qquad (6)$$

where $P_A{}^e$ are $P_B{}^e$ are the equilibrium pressures for reactant A and for product B, respectively.

If the rate of the isomerization reaction is controlled by the adsorption of A, step (3a), the overall reaction rate v per unit surface area of the catalyst is expressed by

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$$v = -\frac{N_0 V}{SRT} \cdot \frac{dP_A}{dt} = \frac{\overrightarrow{k}_a (P_A - P_B/K)\,[S]_0}{1 + (\overleftarrow{k}_b/\overrightarrow{k}_b) K_B P_B}, \quad (7)$$

where N_0, R, and T are Avogadro's number, gas constant, and the absolute temperature, and V, S, and $[S]_0$ are the volume of the reaction vessel, the surface area of the catalyst used, and the number of the adsorption sites per unit surface area of the catalyst, respectively. The demoninator of Eq. (7) always increases as the reaction proceeds. Then, the integration of Eq. (7) does not yield Eq. (1).

If the rate of the isomerization is controlled by the surface reaction, step (3b), the overall rate v per unit surface area is expressed by

$$v = -\frac{N_0 V}{SRT} \cdot \frac{dP_A}{dt} = \frac{\overrightarrow{k}_b K_A (P_A - P_B/K)}{1 + K_A P_A + K_B P_B} [S]_0. \quad (8)$$

If the numbers of surface species AS and BS are both sufficiently small in comparison with the numbers of the corresponding gas-phase species, the sum of the partial pressures of reactant A, P_A, and of product B, P_B, is a constant which is the total pressure, P_T, as follows:

$$P_A + P_B = P_T. \quad (9)$$

Substitution of Eq. (9) in Eq. (8) gives

$$-\frac{dP_A}{dt} = \frac{[S]_0 SRT}{N_0 V} \cdot \frac{\overrightarrow{k}_b K_A (K + 1)(P_A - P_A^e)/K}{1 + K_B P_T + (K_A - K_B) P_A}. \quad (10)$$

Since the chemical properties of reactant A is similar to those of product B, the adsorption equilibrium constant for A may be so close to that for product B that one can obtain the relation

$$\frac{(K_A - K_B) P_A}{1 + K_B P_T} \ll 1. \quad (11)$$

Expanding of Eq. (10) (neglecting terms of higher order of $(K_A - K_B)P_A/(1 + K_B P_T)$) gives

$$-\frac{dP_A}{dt} = \alpha (P_A - P_A^e) \left\{ 1 - \frac{(K_A - K_B) P_A}{1 + K_B P_T} \right\}, \quad (12)$$

where

$$\alpha = \frac{[S]_0 SRT \overrightarrow{k}_b K_A (1 + K)/K}{N_0 V (1 + K_B P_T)}. \quad (13)$$

Equation (12) can be integrated under the initial condition of $P_A = P_0$ at $t = 0$:

$$\ln \left\{ \frac{P_0 - P_A^e}{P_A - P_A^e} \right\} = \alpha t + \Delta, \quad (14)$$

where Δ is written as

$$\Delta = -\alpha \left\{ \frac{(K_A - K_B) P_A^e t}{1 + K_B P_T} \right\} + \ln \left\{ \frac{1 - (K_A - K_B) P_0/(1 + K_B P_T)}{1 - (K_A - K_B) P_A/(1 + K_B P_T)} \right\}. \quad (15)$$

Making use of inequality (11) and expanding Eq. (15), one has a simplified equation as follows:

$$\Delta = \frac{K_A - K_B}{1 + K_B P_T} (P_A - P_0 - P_A^e t). \quad (16)$$

In order to estimate the second term Δ in Eq. (14), one can use the value of P_A obtained from the zero-order approximate equation which is given on the supposition that Δ is 0 in Eq. (14). One obtains

$$P_A = P_A^e - (P_A^e - P_0) \exp(-\alpha t). \quad (17)$$

Substitution of Eq. (17) in Eq. (16) gives

$$\frac{d\Delta}{dt} = -\frac{(K_A - K_B)}{1 + K_B P_T} \cdot \alpha \cdot P_A. \quad (18)$$

From Eqs. (1), (14), and (18), one obtains

$$k = \alpha \left\{ 1 - \frac{(K_A - K_B) \bar{P}_A}{1 + K_B P_T} \right\}, \quad (19)$$

where $\bar{P}_A$ is the average of P_A during the reaction. The first-order rate equation (1) is approximately satisfied because the change of $(K_A - K_B)P_A/(1 + K_B P_T)$ during the reaction may be neglected in comparison with unity from inequality (11).

In the reactions (*1–6*) described previously, the change of $(K_A - K_B)P_A/(1 + K_BP_T)$ was smaller than unity so that k did not depend on P_A and on time. Then a special interest occurs when K_A is equal to K_B:

$$K_A = \frac{\overrightarrow{k}_a}{\overleftarrow{k}_a} = K_B = \frac{\overleftarrow{k}_c}{\overrightarrow{k}_c} = K_0. \qquad (20)$$

Substitution of Eq. (20) in Eq. (4) gives

$$K = \overrightarrow{k}_b/\overleftarrow{k}_b. \qquad (21)$$

By making use of expression (13) for α and substitution of Eq. (20) in Eq. (19) one obtains

$$k = \frac{[S]_0 SRTK_0\,(\overleftarrow{k}_b + \overrightarrow{k}_b)}{N_0V(1 + K_0P_T)}. \qquad (22)$$

The specific rate r defined by the following equation is useful for comparison with the rate of an ordinary chemical reaction:

$$r = N_T/S, \qquad (23)$$

where $N_T = N_0P_TV/RT$ is the total number of molecules in the reaction vessel. Substitution of Eq. (22) in Eq. (23) gives

$$r = (\overleftarrow{k}_b + \overrightarrow{k}_b)\,\frac{K_0P_T}{1 + K_0P_T}\,[S]_0. \qquad (24)$$

The relation between the specific rate r and the total pressure P_T expressed by Eq. (24) has been observed in the *orth–para*-hydrogen conversion over γ-alumina (*1*) and in the isomerization of 1-butene over Ce–Y zeolite (*2*).

In the kinetic treatment on the first-order rate equation expressed by Eq. (1) for the catalytic isomerization published previously (*1, 7, 8*), the authors supposed that there is no difference between the adsorption behaviors of the reactant and the product. In the present paper the general kinetic treatment was performed and the author determined the condition under which the kinetic behavior is expressed approximately by Eq. (1).

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